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Few studies have investigated tillage effects on alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] degradation. Objectives here were to evaluate kinetics and mechanisms of alachlor degradation in surface (0–5 cm) Dundee silt loam (fine-silty, mixed, thermic, Aeric Ochraqualf) from plots managed for 7 years as conventional tillage (CT) or no-tillage (NT) soybeans (*Glycine max* L.). In experiment I, incubations ranged from 0 to 54 days after ^{14}C -ring-labeled alachlor ($4.44 \mu\text{mol kg}^{-1}$) application. In experiment II, soil was incubated (10 g:3 mL of CaCl_2) with ^{14}C -labeled alachlor (14.8 or $111.2 \mu\text{mol L}^{-1}$) from 1 to 25 days. Soils in experiment I were extracted with methanol and in experiment II were sequentially desorbed with 0.01 M CaCl_2 and methanol and then oxidized to measure unextractable ^{14}C . Mineralization of alachlor was more rapid in NT. Methanol-extractable and CaCl_2 -desorbable alachlor declined during incubation for both tillage treatments, with a corresponding increase in methanol-unextractable ^{14}C . Tillage did not influence the initial disappearance of alachlor (half-life ≈ 6.5 days) but did affect metabolite transformations. Alachlor sorption was more rapid in NT, accompanied by less CaCl_2 -desorbable and more methanol-extractable alachlor and metabolites. Unextractable ^{14}C was also greater in the NT soil. Acidic metabolites accumulated in both tillage soils.

Keywords: *Herbicide; alachlor; no-tillage; plant residue; dissipation; sorption*

INTRODUCTION

Alachlor is a soil-applied chloroacetamide herbicide widely used in soybeans under a variety of tillage and crop residue management systems. A few field studies have evaluated alachlor dissipation in reduced tillage soils (Helling et al., 1988; Gaynor et al., 1992; Jones et al., 1990), but because of wide variability of data in those studies, clear conclusions concerning the effects of tillage were not demonstrated. Therefore, field data quantifying the kinetics of alachlor dissipation in conservation tillage systems are very limited. The half-life of alachlor measured in no-tillage field soils was ca. 39 and 11 days in two consecutive years (Helling et al., 1988). This range of values is similar to that reported for conventionally tilled soils (14–28 days) (Sharp, 1988; Yen et al., 1994). Alachlor dissipation was more rapid in no-tillage than in conventional tillage field soils and in soils which were covered with wheat straw, but dissipation kinetics were not quantified (Jones et al., 1990). Gaynor et al. (1990) measured little difference in alachlor dissipation among ridge tillage, no-tillage, and conventional tillage systems. Although alachlor can degrade rapidly (half-life 23–66 days) in surface soils under laboratory conditions (Pothuluri et al., 1990; Yen et al., 1994), under field conditions, lateral (Sauer and Daniel, 1987; Gaynor et al., 1992; Isensee and Sadeghi, 1993) and vertical movement (Isensee et al., 1990; Clay et al., 1992) in water (water solubility 242 mg L^{-1} , 25°C) and volatilization (vapor pressure $1.6 \times 10^{-5} \text{ mmHg}$, 25°C) (Helling et al., 1988; Gish et al., 1995) also contribute to alachlor dissipation. Interception by plant residues (Erbach and Lovely, 1975; Banks and Robinson, 1986) and sorption to organic components in soil (Locke, 1992) also influence herbicide efficacy and persistence in

reduced-tillage soils. Numerous studies have found that pesticides, including alachlor (Bollag et al., 1986), or transformation products interact with humic and fulvic acids to form bound residues (for a review, see Bollag et al., 1992). Other products of alachlor metabolism, such as [(2,6-diethylphenyl)(methoxymethyl)amino]-oxoacetic acid (i.e., oxanilic acid) and 2-[[[(2,6-diethylphenyl)methoxy]methylamino]-2-oxoethanesulfonic acid (i.e., sulfonic acid), are more polar than alachlor and have been detected in groundwater (Baker et al., 1993).

First-order kinetics have been used to describe alachlor degradation in soil (Pothuluri et al., 1990). While chemical hydrolysis of alachlor has been reported (Hargrove and Merkle, 1971), research supports microbial metabolism as the primary mechanism of chloroacetamide degradation (e.g., Pothuluri et al., 1990; Sharp, 1988). Two major pathways of chloroacetamide metabolism have been demonstrated in soil: glutathione (GSH) conjugation (Lamoureux and Rusness, 1989; Feng, 1991) and hydrolysis of the amine group by amidases or arylacylamidases (Novick et al., 1986). Glutathione *S*-transferase (GST) mediates the conjugation of glutathione with a chloroacetamide resulting in the formation of an acetamide-*S*-glutathione conjugate. The *S*-glutathione conjugate undergoes further peptide cleavage to the cysteine conjugate intermediate and then to polar compounds such as oxanilic acid, sulfonic acid, and sulfinylacetic acid.

Enzymatic cleavage via arylacylamidase to form aniline may not be possible for certain chloroacetamide herbicides such as alachlor without prior *N*-dealkylation as discussed above. In the case of alachlor, this product, 2-chloro-*N*-(2,6-diethylphenyl)acetamide, i.e., des(methoxymethyl)alachlor, may then subsequently serve as substrate for arylacylamidases with the potential product being 2,6-diethylaniline, which has been detected in groundwater (Potter and Carpenter, 1995) and surface water (Rostad et al., 1989). Degradation to

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Table 1. TLC and HPLC Conditions

chromatography system	solvent system/mobile phase	compound	R _f or t _R (min)
TLC hexane	hexane:ethyl acetate:methylene chloride (6:3:1, v:v:v)	2,6-diethylaniline	0.53
		des(methoxymethyl)alachlor	0.63
		alachlor	0.82
		acidic polar metabolites (e.g., sulfonic and oxanilic acids, glutathione, glycylcysteine)	origin
TLC butanone	butanone:acetic acid:H ₂ O (10:1:1, v:v:v)	cysteine	0.33
		sulfonic acid	0.47
		oxanilic acid	0.65
		hydroxyalachlor	0.98
		alachlor	0.98
TLC acetonitrile	acetonitrile:H ₂ O:NH ₄ OH (44:9:1)	cysteine	0.46
		oxanilic acid	
		sulfonic acid	0.56
HPLC	H ₂ O (1% acetic acid):acetonitrile gradient of 70:30 (initial) to 40:60 (final), 1 mL min ⁻¹ flow rate	alachlor	0.95
		sulfonic acid	2.2
		oxanilic acid	2.6, 4.3
		glutathione-alachlor conjugate	4.9
		cysteine-alachlor conjugate	5.4
		glycylcysteine-alachlor conjugate	5.8
		2,6-diethylaniline	8.7
		des(methoxymethyl)alachlor	10.1
		alachlor	14.4
	1 mL min ⁻¹ flow rate		

anilines may also result in increased binding to soil (Bollag et al., 1978), particularly to organic components rather than to clay minerals (Hsu and Bartha, 1974).

In many conservation management systems, soils typically have elevated organic carbon levels or accumulated plant residues at the soil surface and associated higher moisture contents and microbial populations (e.g., Doran, 1980; Linn and Doran, 1984; Reddy et al., 1995). However, few studies have evaluated tillage effects on alachlor degradation. The objectives of the present study were to evaluate and characterize the kinetics and mechanisms of alachlor degradation in surface soil from two long-term soybean tillage systems and relate degradation to sorption and binding. Two experiments were included in this study. The objective of experiment I was to assess tillage effects on mineralization and metabolite formation in soil. In experiment II, the objective was to relate the degradation information gained in experiment I to alachlor sorption and binding processes.

MATERIALS AND METHODS

Soil. Laboratory studies were conducted using surface (0–5 cm) Dundee silt loam (fine-silty, mixed, thermic, Aeric Ochraqualf) soils. The soils were collected at random from five replications of long-term (7 years) conventional tillage (CT) or no-tillage (NT) soybean plots near Stoneville, MS. Soil in the CT plots was disked twice in the spring before planting, while the NT soil was not disturbed. The soils had no recent (at least 7 years) history of alachlor, but all plots received glyphosate to kill existing vegetation at planting and 0.56 kg ha⁻¹ metribuzin as a preemergence herbicide. The soil was sampled in the spring after the CT soils were disked but prior to herbicide application.

For each tillage system, samples from the five replications were composited, air-dried, ground, sieved (2 mm), and stored at 4 °C until use. For NT and CT soils, respectively, pHs (1: 1, 0.01 M CaCl₂) were 5.13 and 5.29 and organic carbon contents were 22.0 and 11.6 g kg⁻¹.

Chemicals. Technical grade alachlor (97% purity) and 2,6-diethylaniline (99%) were purchased from Chem Service, Inc., West Chester, PA. Uniformly ring-labeled [¹⁴C]alachlor, obtained from Monsanto Corp., St. Louis, MO, was 99% pure with a specific activity of 430 kBq mmol⁻¹. Radiolabeled sulfonic acid and conjugates of alachlor were synthesized from ¹⁴C-labeled alachlor purchased from Sigma Chemical Co., St. Louis, MO (97% purity, specific activity 1010 kBq mmol⁻¹),

according to a method described by Feng and Patanella (1988). Des(methoxymethyl)alachlor was obtained from R. Johnson (USDA-ARS, New Orleans, LA), and oxanilic acid was obtained from J. Pothuluri (NCTR-FDA, Jefferson, AR).

Experiment I. Fifty grams of air-dried soil from each tillage treatment was weighed into biometer flasks (Bartha and Pramer, 1965) and treated with 15 mL of [¹⁴C]alachlor (14.8 μmol L⁻¹) to attain a final soil concentration of 4.44 μmol kg⁻¹ (72.0 kBq kg⁻¹), or ca. 2.68 kg ha⁻¹ if extrapolated to a field basis. The samples were brought to uniform moisture (0.35 g/g of oven-dried soil, ca. field capacity) and incubated for 1 h or 1, 4, 12, 18, 25, 40, or 54 days, with each sampling time run in triplicate. Mineralization was evaluated by sampling 1 M NaOH traps at weekly intervals from the flask sidearm. At the end of each designated incubation interval, the soil was quantitatively removed, extracted twice with 100 methanol/0.15% (w/v) Na₂SO₄ (2:1 extract:soil; first and second extractions 24 and 3 h, respectively), air-dried, and combusted to measure methanol-unextractable ¹⁴C (Oxidizer Model 306, Packard Instruments, Downers Grove, IL). The ¹⁴C in duplicate aliquots of the combined extracts was measured by liquid scintillation counting (liquid scintillation counter Packard Model 4430). The extracts were rotary evaporated and filtered through C-18 solid-phase extraction (SPE) columns (J.T. Baker Chemical Co., Phillipsburg, NJ). Aliquots of filtrate were counted to determine the fraction of ¹⁴C not retained on the SPE column. Extract components adsorbed to the solid-phase columns were eluted with 2 mL of acetonitrile.

Subsamples (50 μL) of the acetonitrile extracts were spotted on silica gel TLC plates (250 μm, with preadsorbant) and developed to 10 cm with a hexane solvent system (Table 1) (Liu et al., 1989). Distribution of ¹⁴C was determined using a Bioscan System 200 linear imaging scanner (Bioscan Inc., Washington, DC).

Additional subsamples of soil extract were analyzed with HPLC using UV (multiwavelength programmable, Model 490E, Waters, Inc., Milford, MA) and liquid scintillation (β-ran flow-through system, Model 2, INUS Systems, Inc., Tampa, FL) detectors and a μBondapak reverse-phase (Waters, Inc.) column (Table 1).

Further verification of extracted constituents was by secondary TLC systems. Soil extract samples were concentrated and fractionated with HPLC. Each fraction was diluted in 50 mL of acidified water, filtered through a C-18 SPE column, eluted with 3.0 mL of 90% ACN, and concentrated to 0.5 mL. Subsamples of each fraction were analyzed with hexane, butanone, and acetonitrile TLC systems (Table 1).

Experiment II. Ten grams air-dried soil was placed into 30 mL glass beakers and treated with 3 mL of [¹⁴C]alachlor (14.8 or 111.2 μmol L⁻¹) in 0.01 M CaCl₂. The beakers were

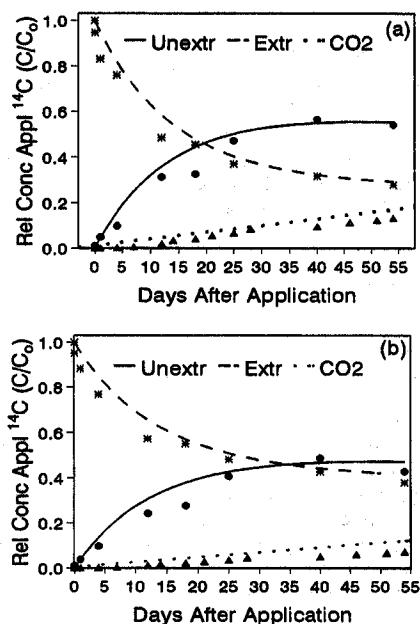


Figure 1. Total extractable ^{14}C , unextractable ^{14}C , and alachlor mineralization (as $^{14}\text{CO}_2\text{-C}$) during incubation of (a) no-tillage and (b) conventional tillage soils. Curves represent data predicted by models, and symbols represent actual mean values.

covered, and samples were incubated at 25 °C for 1, 4, 11, or 25 days. There were three replications of each combination of tillage and alachlor concentration for each incubation time. After incubation, the soil was quantitatively rinsed into a 25 mL glass centrifuge tube with 15 mL of 0.01 M CaCl_2 . The samples were shaken for 1 min and centrifuged, and 10 mL supernatants were removed. Aliquots of the supernatants were counted for ^{14}C . This fraction was termed solution ^{14}C because no extended period of equilibration was used to desorb the measured radioactivity. Ten milliliters of herbicide-free 0.01 M CaCl_2 was added to replace the removed supernatants, and the samples were shaken for 24 h. The 24 h desorption with CaCl_2 was repeated twice. The cumulative radioactivity removed in the three sequential desorption extractions was termed CaCl_2 -desorbable ^{14}C . After extraction with 0.01 M CaCl_2 , the soils were extracted twice with 100 mL methanol/0.15% (w/v) Na_2SO_4 (2:1 extract:soil; first and second extractions 24 and 3 h, respectively). This fraction was termed methanol-extractable ^{14}C . The soil was allowed to air-dry, and 0.3 g subsamples were combusted to determine unextractable ^{14}C .

Statistical Analyses. A split plot design was used in both experiments. In experiment I, the main unit was a completely randomized factorial of the two tillage treatments with time of destructive sampling as a subunit. In experiment II, the main unit was a completely randomized factorial of tillage and initial alachlor concentration with time as a subunit. Analysis of variance statistical procedures were used to evaluate effects of tillage, initial alachlor concentration, and time after application, and Fishers *l*sd test was used to separate means. Nonlinear regression was used to estimate model parameter coefficients.

RESULTS AND DISCUSSION

Experiment I. Extractable, Unextractable, and Mineralized ^{14}C Fractions. Total methanol-extractable ^{14}C declined rapidly during the first 10–15 days, with a half-life of about 10 days for both soils (Figure 1). Tillage differences in methanol-extractable ^{14}C were not discernable until 12 days after application when less ^{14}C was measured in extracts from the NT soil (48.5%, NT; 57.3%, CT) (Figure 1). The decline in methanol-extractable ^{14}C corresponded to an increase in unextractable ^{14}C and $^{14}\text{CO}_2$ evolution (Figure 1), both of

which were higher for NT at all times greater than ca. 7 days. In another study (Reddy et al., 1995) using soil from the same field plots, we determined that the no-tillage had higher bacterial populations (e.g., total Gram-negative and fluorescent pseudomonads) and enzyme activities, and this may have contributed to the tillage effect on mineralization for soils in the present study. Unextractable ^{14}C steadily increased throughout the incubation period and was the single largest pool (43–54%) of applied ^{14}C for both tillage soils at the end of the study period (Figure 1). Although cumulative mineralization ($^{14}\text{CO}_2\text{-C}$) accounted for only 7% (CT) or 13% (NT) of applied alachlor during the 54 day incubation (Figure 1), it is higher than alachlor mineralization rates reported by others: 2% after 32 days (Levanon, 1993), 3.3% after 39 days (Zablotowicz and Dzantor, 1994), and <1.7% (Yen et al., 1994). Mass balance (sum of extractable, unextractable, and mineralized fractions of applied ^{14}C) averaged over time and tillage was 89%, similar to that observed in other studies (e.g., Yen et al., 1994).

The ^{14}C systems (Figure 1) were well-described assuming first-order reactions, including reversible mass transfer between extractable and unextractable pools:

$$dE/dt = -(k_d + k_r)E + k_f U \quad (1a)$$

$$dU/dt = k_f E - k_r U \quad (1b)$$

$$dV/dt = k_d E \quad (1c)$$

where E , U , and V are fractions of applied ^{14}C existing in extractable, unextractable, and mineralized forms, respectively, and k_f (d^{-1}), k_r (d^{-1}), and k_d (d^{-1}) are the first-order rate constants for reversible binding, release, and mineralization, respectively. Equations 1a,b represent a two-compartment model for ^{14}C substrate mineralization in which methanol-extractable and unextractable fractions correspond to labile and nonlabile compartments (Hamaker and Goring, 1976). The integrated forms of eqs 1 may be fit simultaneously to the respective data sets.

The results for NT and CT soils are shown in Figure 1. Best-fit parameters were $k_f = 0.046 \pm 0.005$, $k_r = 0.025 \pm 0.006$, and $k_d = 0.006 \pm 0.001$ (NT) and $k_f = 0.040 \pm 0.005$, $k_r = 0.035 \pm 0.008$, and $k_d = 0.004 \pm 0.001$ (CT). The R^2 values for the NT and CT data were 0.986 and 0.989, respectively, despite complications of incomplete ^{14}C mass balance.

Extractable Alachlor and Total Extractable Metabolites. Analysis of methanol extracts with HPLC indicated that tillage did not influence the disappearance of alachlor (Figure 2). The pattern followed typical first-order kinetics:

$$dS/dt = -k_D S \quad (2)$$

where S is the mass of extractable alachlor. Best-fit k_D values were 0.106 ± 0.005 (CT) and 0.106 ± 0.008 (NT), giving R^2 values of 0.995 and 0.998, respectively. Thus, alachlor disappearance was most rapid during the first 12 days (half-life ≈ 6.5 days), alachlor levels declining from only 26% to <5% of applied during the remainder of the study (Figure 1). This trend was verified using the hexane TLC system.

Alachlor sorption in the Dundee soils has been shown to be time-dependent and well-described by a kinetic model which allowed for slowly reversible partitioning between methanol-extractable and unextractable frac-

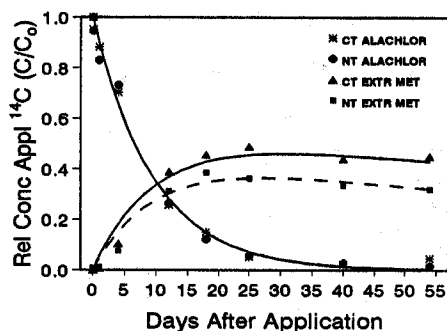


Figure 2. Effect of tillage on alachlor disappearance (HPLC analysis) and total extractable metabolite accumulation. Symbols represent actual means, and curves represent values predicted by a model.

tions (Locke, 1992). Therefore, initial attempts to model alachlor disappearance in the NT and CT soils assumed reversible partitioning and degradation in the extractable fraction (analogous to eq 1a). However, parameter estimates exhibited large uncertainties.

High uncertainty in parameter values was also obtained when fitting two-compartment formulation to data for extractable metabolites. Instead, appearance/disappearance of total extractable metabolites, M , was adequately described by

$$dM/dt = k_F S = k_D M \quad (3)$$

where k_F (d^{-1}) is the rate constant for formation of metabolites from substrate alachlor and k_D (d^{-1}) is the dissipation rate constant. Solutions to eq 3 shown in Figure 2 were based on the first-order model for extractable alachlor. Values of k_F and k_D were, respectively, 0.047 ± 0.004 and 0.007 ± 0.003 (NT) and 0.056 ± 0.005 and 0.003 ± 0.003 (CT), indicating that total metabolites were forming more rapidly and dissipating more slowly in the CT soil.

These k_F values were approximately half the k_D values for alachlor disappearance. Thus, the appearance of metabolites could not fully account for the disappearance of alachlor, suggesting accumulation of alachlor/alachlor residues in the methanol-unextractable fraction.

HPLC and TLC Fractionation of Methanol Extracts. Even though tillage did not influence the disappearance of extractable alachlor, analysis of methanol extracts with HPLC indicated tillage effects with respect to the various metabolites. Principal metabolites included compounds coeluting with the sulfonic acid peak (HPLC peak 1, Figure 3a; Figure 4a) and the oxanilic acid peak (peak 2, Figure 3b; peak 3, Figure 3c; Figure 4a), with oxanilic acid existing as two rotational isomers, stable at room temperature and exhibiting different HPLC retention times (Pomes et al., 1993). However, sulfonic acid and sulfinylacetic acids may be difficult to resolve by HPLC (Feng, 1991). Alachlor-glutathione conjugate and alachlor-glycylcysteine had retention times similar to one of the oxanilic acid isomers, but TLC analysis with the butanone system verified that these were not present in the soil extracts. Several other metabolites, including one coeluting with des(methoxymethyl)-alachlor, appeared in much smaller quantities (<3% of total applied ^{14}C). In general, quantities of metabolites coeluting with the sulfonic and oxanilic acids were higher in the CT samples throughout the study (Figure 3). Maximum concentrations existed from about 18 to 40 days of incubation, beyond which time metabolite degradation exceeded formation.

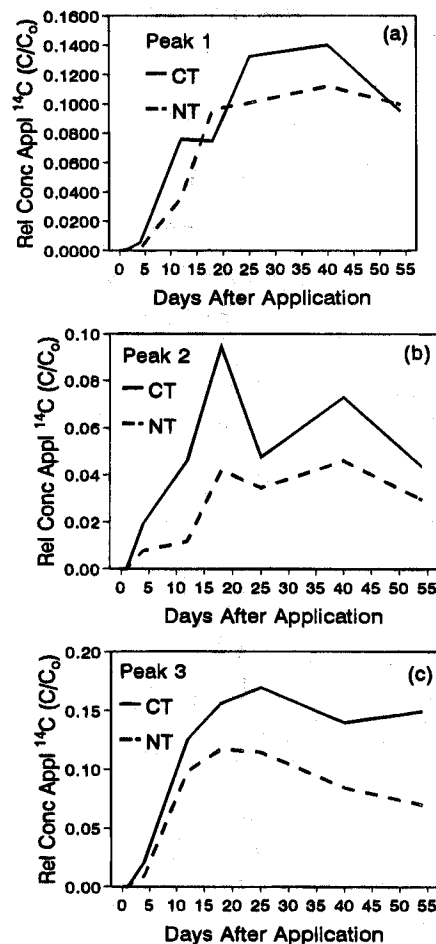


Figure 3. Effect of tillage on metabolite appearance as measured by HPLC: (a) peak 1 (t_R 2.2 min), (b) peak 2 (t_R 2.6 min), and (c) peak 3 (t_R 4.3 min).

Analysis of soil extracts by TLC generally supported the HPLC results. Figure 4b shows TLC hexane chromatograms for the NT soil. In the hexane system, the principal metabolite peak occurred at the origin, consistent with immobility expected for polar, acidic character (sulfonic and oxanilic acids). Average concentration of these acidic metabolites during the period from 18 to 54 days was greater in the CT samples (24.8%, SE 0.66, compared to 16.6%, SE 0.38, of applied ^{14}C). Minor peaks (<4%, no tillage difference) included those with R_f values corresponding to hydroxy alachlor, des(methoxymethyl)alachlor, and 2,6-diethylaniline. One major peak (CT 6.08%, SE 0.39; NT 5.44%, SE 0.39) at R_f 0.39 was unidentified (Figure 4b).

To further evaluate the composition of methanol extracts, metabolites were grouped according to polarity as indicated by HPLC and TLC separations. Soil extracts were fractionated by HPLC and evaluated with three TLC solvent systems. Metabolites eluted early by HPLC were polar (remained at origin in the hexane system) (Figure 4b) with ca. 80% exhibiting R_f s consistent with sulfonic and oxanilic acid in the butanone and acetonitrile TLC systems. Those fractions collected at longer retention times were predominantly nonpolar. The data for the metabolites collected in the early range were added to data of metabolites not retained by the SPE C-18 column during processing, and the two groups were labeled polar. These are compared to the nonpolar metabolites in Figure 5. Polar metabolites rapidly accumulated from 4 to 12 days after alachlor application and then leveled off for both tillage treatments (Figure

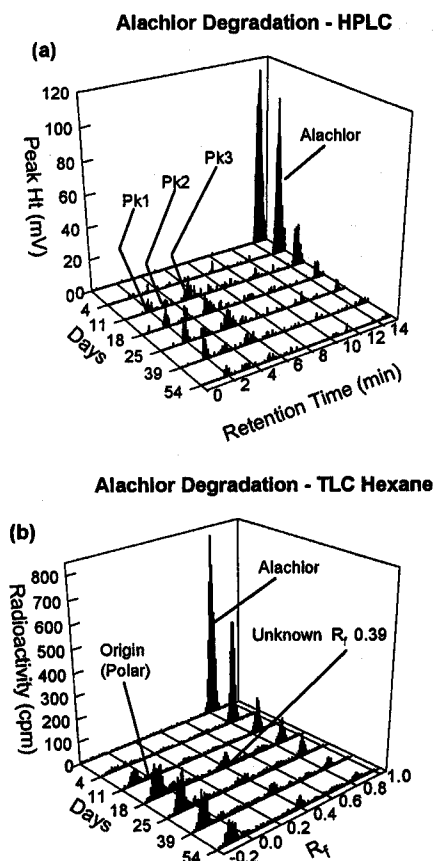


Figure 4. Alachlor degradation in NT soil: (a) days 0–54 as analyzed by HPLC and (b) days 0–54 as analyzed by TLC hexane solvent system.

5). The polar metabolites were higher in the CT extracts during the entire incubation period, indicating slower metabolism.

Appearance and disappearance of these pools of metabolites were well-described using a model analogous to eq 3. The modeled data are shown in Figure 5. Best-fit parameters for polar, acidic metabolites were $k_F = 0.047 \pm 0.004$ and $k_D = 0.004 \pm 0.003$ (CT) and $k_F = 0.037 \pm 0.003$ and $k_D = 0.006 \pm 0.003$ (NT). Thus, the formation rate constant for such metabolites as sulfonic and oxanilic acids was somewhat faster in CT; however, dissipation rate constants in the CT and NT soils were slow, indicating tendency for such compounds to accumulate. Corresponding parameters for nonpolar metabolites were $k_F = 0.003 \pm 0.001$ and $k_D = 0.005 \pm 0.018$ (CT) and $k_F = 0.005 \pm 0.001$ and $k_D = 0.026 \pm 0.013$ (NT). In contrast to the polar metabolites, k_{DS} exceeded k_{FS} , especially for the NT soil, consistent with negligible accumulation of nonpolar metabolites in these soils.

It is evident that the acidic polar metabolites generated via glutathione conjugation were the major extractable alachlor metabolites in these Dundee soils. Similar percentages of the acidic metabolites have been observed under higher alachlor soil concentrations (Zablotowicz and Dzantor, 1994). In contrast, studies by Yen et al. (1994) indicated slower alachlor degradation rates with a lower accumulation of the acidic metabolites (<10%). However, studies by Baker et al. (1993) have indicated that alachlorsulfonic acid is the major form of alachlor detected in ground water, and they hypothesized that it is both persistent and highly mobile.

Initial metabolism of alachlor in experiment I was not influenced by tillage, as indicated by the similarity in

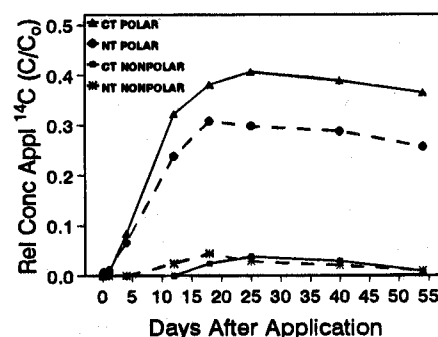


Figure 5. Effect of tillage on total polar and nonpolar metabolite accumulation. Symbols represent actual means, and curves represent values predicted by a model.

degradation curves (Figure 2). However, once initial breakdown occurred, reactions in the CT soils were slower, resulting in a longer residence time for the metabolites (Figure 2). In NT, a greater portion was converted to the unextractable and mineralized fractions. In both tillage soils during 18–54 days, the nonpolar extractable metabolite component averaged <4% of applied ^{14}C . The nonpolar portion included metabolites such as des(methoxymethyl)alachlor and 2,6-diethylaniline which would be likely candidates for polymer binding in the soil humic material (Bollag et al., 1992). The low proportion attributed to nonpolar materials would lend credence to the argument that these materials were rapidly assimilated into the unextractable portion of the soil material.

Experiment II. Some trends observed in experiment I were corroborated by the second study. Extractable ^{14}C was separated into three fractions reflecting increasing retentivity: solution ^{14}C (in solution at the end of each incubation period), CaCl_2 -desorbable ^{14}C , and methanol-extractable ^{14}C (after desorption with CaCl_2). The ^{14}C in solution decreased slightly after 24 h for CT soil, while it remained the same throughout the 25 day period in NT soil (Table 2). For both soils, apparent equilibrium between solution and adsorbed ^{14}C was achieved after 24 h and are consistent with the kinetics of alachlor sorption measured in the same soil by Locke (1992). In that study, the Freundlich parameters ($k_{\text{Freund}}, 1/n$) for NT and CT, respectively, were 5.62 (0.87) and 3.61 (0.87) at 24 h and 5.88 (0.89) and 4.05 (0.88) at 96 h. Based upon results from experiment I in the present study, most of the material sorbed during the latter stages (>4 days) was not alachlor, and use of the solution ^{14}C to calculate sorption coefficients for longer time periods must be done with caution. For NT, less ^{14}C in solution at the end of each incubation period reflected a higher sorption capacity (Table 2). The tillage effect on the CaCl_2 -desorbable ^{14}C fraction was consistent over the 25 day period (values averaged over time in Table 3) with a higher percentage measured in CT for both initial herbicide concentrations. During the early part of the incubation period (1 and 4 days), there was more methanol-extractable ^{14}C in NT, but for days 11–25, there was no tillage difference (Table 2). However, there was higher unextractable ^{14}C in NT throughout the study period (Table 2).

For both tillage soils, methanol-extractable ^{14}C fractions decreased with time (Table 2). CaCl_2 -desorbable ^{14}C also decreased with incubation time, but there was no interaction of time and tillage, unlike the case of the methanol-extractable fraction. The decrease in the methanol-extractable and CaCl_2 -desorbable fractions reflected degradation as well as a decreasing extract-

Table 2. Effect of Tillage and Incubation Time on Solution ^{14}C , Methanol-Extractable ^{14}C , and Methanol-Unextractable ^{14}C ^a

incubation interval (days)	solution (% of added ^{14}C)		CaCl ₂ desorbable (% of added ^{14}C)		methanol-extractable (% of added ^{14}C)		methanol-unextractable (% of added ^{14}C)	
	CT	NT	CT	NT	CT	NT	CT	NT
1	37.1a ^b a ^c	27.0b b	25.9 ^d	24.5	22.7a ^b b ^c	29.4a a	11.3d ^b b ^c	16.7c a
4	35.6ab a	26.9b b	25.0	21.8	20.6b b	25.8b a	14.4c b	18.5c a
11	34.8b a	27.6ab b	18.3	16.1	16.4c b	17.4c a	20.4b b	28.5b a
25	34.4b a	28.8a b	13.8	10.4	11.5d a	11.8d a	28.7a b	36.3a a

^a Values are averaged over initial herbicide concentration. ^b Within a column (for each category), means followed by the same letter are not significantly different (Fisher lsd $\alpha = 0.05$). ^c Within a row (for each category), means followed by the same letter are not significantly different (Fisher lsd $\alpha = 0.05$). ^d Interaction of tillage and time of sampling was not significant. Individual means are shown to provide mass balance of the four fractions.

Table 3. Effect of Initial Solution Concentration and Tillage on ^{14}C Desorbable in CaCl₂ and Extractable in Methanol^a

tillage	CaCl ₂ desorbable (% of added ^{14}C)		methanol-extractable (% of added ^{14}C)	
	14.8 μM	111.2 μM	14.8 μM	111.2 μM
CT	18.5a ^b b ^c	23.0a a	16.0b b	18.7b a
NT	17.0b b	19.5b a	19.6a b	23.4a a

^a Values are averaged over sampling times. ^b Within a column (for each category), means followed by the same letter are not significantly different (Fisher lsd $\alpha = 0.02$). ^c Within a row (for each category), means followed by the same letter are not significantly different (Fisher lsd $\alpha = 0.01$).

Table 4. Effect of Initial Solution Concentration and Incubation on ^{14}C Desorbable in CaCl₂ and Extractable in Methanol^a

incubation interval (day)	CaCl ₂ desorbable (% of added ^{14}C)		methanol-extractable (% of added ^{14}C)	
	14.8 μM	111.2 μM	14.8 μM	111.2 μM
1	25.3a ^b a ^c	25.1a a	25.6a a	26.5a a
4	21.8b	25.0a	21.4b	24.9b
11	13.9c b	20.5b a	13.8c b	20.1c a
25	9.94d b	14.3c a	8.65d b	14.6d c

^a Values are averaged over tillage treatment. ^b Within a column (for each category), means followed by the same letter are not significantly different (Fisher lsd $\alpha = 0.01$). ^c Within a row (for each category), means followed by the same letter are not significantly different (Fisher lsd $\alpha = 0.01$).

ability with time. A corresponding increase in methanol-unextractable herbicide residues in both tillage treatments (Table 2) supports this reasoning.

Some significant effects of initial solution concentration were observed. With the exception of the 24 h samples, a greater portion of ^{14}C in the higher initial alachlor concentration was CaCl₂-desorbable and methanol-extractable when compared to the lower alachlor concentration (Table 4). This trend was consistent for both CT and NT (Table 3). Unextractable ^{14}C was greater with the lower initial concentration (25.9% vs 17.8%). These data were consistent with sorption nonlinearity (Locke, 1992) and indicate that a greater portion of the herbicide or metabolites was labile at the higher concentration. Increased persistence with higher application rate has been observed by other researchers. Felsot and Dzantor (1990) studied alachlor metabolism in soil at initial application concentrations ranging from 10 to 1000 mg kg⁻¹. At 28 days after application,

unextractable ^{14}C was higher and extractable ^{14}C was lower at the lower initial application concentrations.

SUMMARY AND CONCLUSIONS

Increased organic carbon in the NT and associated enhanced microbial activity may have been the soil characteristics which contributed most to tillage differences in alachlor degradation and sorption. Evidence supporting greater retention of herbicide residues in NT included lower quantities of CaCl₂-desorbable ^{14}C and a greater methanol-unextractable portion of the applied ^{14}C .

Tillage did not significantly affect initial alachlor degradation, which followed first-order kinetics. A half-life of 6.5 days in both CT and NT is less than that reported in the field. However, these results are in general agreement with field studies showing that tillage did not influence alachlor dissipation (e.g., Gaynor et al., 1992), although many factors other than degradation contribute to dissipation in the field.

Tillage did influence the pattern of alachlor residue metabolism. In the NT soil, degradation of the metabolite coeluting with the sulfonic acid standard was more rapid. Also, a greater percentage of the ^{14}C applied to NT was trapped as $^{14}\text{CO}_2$, indicating more rapid herbicide mineralization. The higher methanol-unextractable portion of the applied ^{14}C was likely metabolites incorporated into humic materials by oxidative coupling reactions.

The data from this study could have implications on a field scale. Prolonged residence time of alachlor or alachlor residues at the soil surface increases the potential for removal in surface runoff, depending on the affinity of the alachlor/residues for the soil organic material. Slower metabolism of polar metabolites in CT might increase the potential for these compounds to move into groundwater where they may be less vulnerable to degradation. Enhanced degradation of metabolites in the NT soil might offset any problems associated with longer residence time at the soil surface.

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